Risk Assessment of Mildly Flammable Refrigerants with low GWP for Heat Pumps

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ABSTRACT

Given the growing demand for cooling, and taking into account the impact of global warming associated with cooling technologies the global climate commitment to reduce the impact of fluorinated gases and the regulations controlling their use in the European Union has increased . This thesis investigates new refrigerants that have been recently proposed to meet the demands of the heat pumps in the refrigeration industry, which must satisfy the legislative requirements of the F-gas Regulation and facilitate meeting the goals of Montreal and Kyoto Agreement.

The fluids R32, R1234ze, R1234yF, R452b and R454b have been theoretically analyzed in comparison with the commonly used fluorinated refrigerant in heat pump: R410A. To compare these refrigerants, an excel sheet has been used to calculate the COP for the different cases studied using the REFPROP computer program to know the thermodynamic data of each fluid. The cases studied are the three different heat pump applications : radiators, radiant floor and fan coil and it has been studied for an evaporator temperature range of -15 to 12 ºC, i.e. the COP has been calculated for eighteen different situations. For all of them, the same conclusion has been concluded: all these five proposed fluids have a higher COP than the fluid to be replaced, R410A. It based on this COP for all the cases studied, the best fluids are R454b and R1234Ze(E). Choosing the fluid R454b as the best alternative because its latent heat and vapour density are higher that R1234ze(E) and therefore the flow and size of the pump is smaller, which generally translates into economic savings.

However, this refrigerant shows flammability characteristics. For this reason, this paper is checked the fluid risk by a risk assessment. For this assessment two scenarios are analyzed by numerical model, Plume Model: outside and inside of 20 m^2 scenario using a 50 kW heat pump. Concluding on the one hand, that in outside conditions a leak would not enter ignition due to the concentration obtained is less than the minimum necessary. In addition from 200 meters of distance the concentration of this fluid would be zero.

And that in the hypothetical case that a jet fire takes place is observed that from 10 meters of the leak there is no more radiation.

On the other hand, for the room scenario the calculated concentration would be 550 g/m^3. This concentration is higher than the acute toxicity exposure limit (435 g/m^3) so it is not safe for a human being to work in the situations described.

GENERAL SUMMARY

FIGURES SUMMARY

TABLES SUMMARY

1 Introduction

1.1 Heat pump

In recent years, with the aggravation of air pollution, depletion of fossil-based energy, the problems of the low heating efficiency and serious pollution from traditional coalfired boilers, heat pump has been becoming an attractive alternative. This is an efficient and non-direct pollution heating technology.

Moreover, the heat pump is safer than traditional systems because there is not danger of gases, it is not necessary a fuel tank and do not emit smokes. [1]

Heat pumps are the preferred alternative to coal-fired boilers for building heating. Common heat pump systems mainly include air, solar and ground source heat pumps.

The advantage of using the heat pump lies in its ability to generate more useful energy (heat energy) than it uses for its operation (electrical energy), being able to produce savings of 70% compared to a traditional heating system such as gas, electricity or diesel. [2]

Presently, photovoltaic assisted heat pump system can be identified as an important area of research. The system involves the favorable integration of photovoltaic modules with a heat pump: the production of heat and electricity with improves performance coefficient and overall efficiency. Compared to the other hot water technologies that use either conventional or non-conventional energy resources, this system is more energy-efficient and reliable because it doesn't need to take electricity from the grid. This is because the photoelectric cell is an electronic device that transforms light energy (photons) into electrical energy (flow of free electrons) through the photoelectric effect, generating photovoltaic solar energy. Its operation is based on a material that presents a photoelectric effect: they take up photons of light and emit electrons. When these free electrons are captured, the result is an electric current that can be used as electricity.

But this technology is development yet due to the low efficient (about 16% for building and 46 % in laboratory) [2]

1.1.1 The operation air-water heat pump

The heat pump is based on the mechanical-compression cycle, it is a refrigeration system that can be reversed to either heat or cool a space. It consists of transporting energy as heat, takes advantage of the ability of cooling fluids, the refrigerants, to release heat when it changes from state using the help of a compressor.

This pump captures energy from external, free and different sources:

- Aerothermal heat pumps: use aerothermal energy (energy contained in the air) to function. They can be of the air-air and air-water type and provide hot or cold air depending on the temperature needs of the space.
- Hydronic heat pumps: those formed by the water-air and water-water systems that climatize the buildings by means of hot water or cold water, generated by the heat pump. The water is distributed in the building by means of a system of pipes, where it is possible to bring heat or cold to the place.
- Geothermal heat pumps obtain the heat from the energy contained in the subsoil and transfer it to the inside of the house. They can be of the type earth-air and earth-water. [3]

This thesis is focused in aerothermal type, the heat taken from the air is transferred to a water circuit for later supply (air-water system). This characteristic makes it an equipment that multiplies the electrical power of the compressor, transporting useful heat in a highly efficient way.

This type of system contains four main parts: a cold source heat exchanger called the evaporator, a compressor, a high-temperature heat exchanger called the condenser and an expansion valve. This system illustrated in Figure 1.

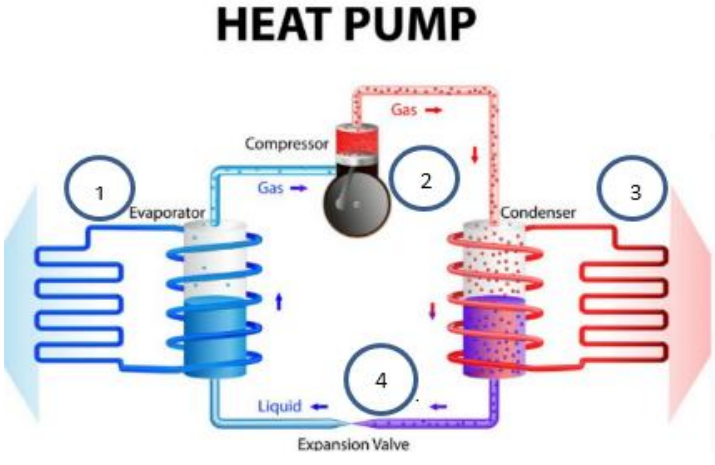


Figure 1- Heat pump system [3]

In a heating process at the first step the refrigerant fluid is at low temperature and low pressure and therefore in a liquid state. The environment air sucked passes through the evaporator (1), where the refrigerant fluid absorbs the heat from the ambient air and changes state (vapor state). At the same time, the air is expelled at a lower temperature.

This vapor that is still at low pressure, passes through the compressor (2) causes an increase in pressure with a consequent increase in temperature. As a result, the steam achieves a high energy state.

This steam is the one that circulates through the condenser (3) located along the boiler where it gives all the energy to the accumulated water, thus returning to a liquid state.

This liquid then passes through the expansion valve (4) to the low-pressure side of the system, and the cycle repeats. [3]

According to the second law of thermodynamics, heat cannot be spontaneously transferred from a colder location to a hotter place without work from an external energy source being applied to the system.

The Figure 2 shows the ideal vapor compression, which represents the change in temperature and entropy that occurs during the cycle.

The area to the left of the bell-shaped curve represents the liquid only phase, vapor lies to the right, and under the curve is a two-phase mixture of liquid and vapor. [4]

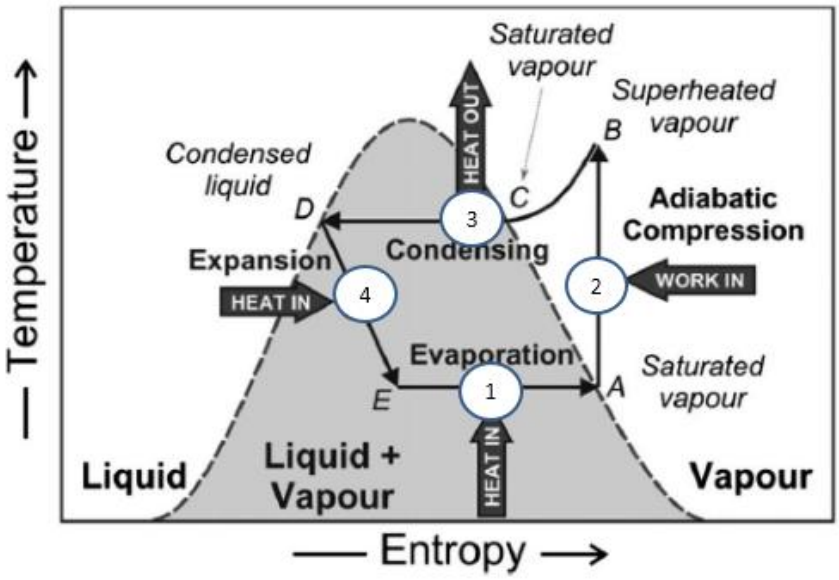


Figure 2- Ideal vapor compression temperature–entropy diagram [4]

The efficiency of refrigeration systems and heat pumps is denoted by its Coefficient Of Performance (COP). The COP is the ratio between energy usage of the compressor and the amount of useful cooling at the evaporator (for a refrigeration installation) or useful heat extracted from the condenser (for a heat pump), heat output to work input. .A system's COP represents its steady-state performance under a set of controlled conditions with defined input and output temperatures.
A high COP value represents a high efficiency. For example, a heat pump operating with a COP=6 will produce 6 kWh of heat for every 1 kWh of electricity supplied.[4]

1.2 Refrigerants diffusion and environmental issues

Refrigerants are substances that can be used in the refrigeration cycle of air conditioning and refrigeration equipment because of their thermodynamic properties. Any substance that changes from liquid to vapor and vice versa, can function as a refrigerant. It depends on the range of pressures and temperatures at which it makes these changes, it will have a useful application.

Nowadays, the globalized world has increased the use of refrigerant gases since they are not only used for food preservation. Some applications of refrigerants are also for the conditioning of spaces to achieve a degree of thermal comfort appropriate for the habitability of a building or means of transport. For the preservation of medicines or other products that degrade with heat. For example, the production of ice or snow, the best preservation of organs in medicine.
For industrial processes that require reducing the temperature of machinery or materials for their correct development. Some examples are machining, the manufacture of plastics, the production of nuclear energy. Use of cryogenics or cooling at very low temperatures, used to liquefy some gases or for some scientific research.
And for internal combustion engines to preserve the engine from breakdowns when temperatures below zero occur. [5]
So, the chances of these gases ending up in the atmosphere are greater.

Since the 1970s, awareness of environmental about refrigerants issues has been growing. This environmental awareness has had many problems for many years due

to economic and production interests, as companies have for many years seen these types of environmental measures as impediments to development. But over time, environmental awareness and sustainability is gradually becoming one of the pillars of the market.[6]

Most conventional refrigerants belonged to the group of chlorofluorocarbons (CFCs) or hydrofluorocarbons (HCFCs). These compounds, in contact with the sun's ultraviolet radiation react with ozone by destroying this protective layer of the atmosphere.

The ozone layer is a fundamental layer of the atmosphere, because it is a natural filter, it protects us from UV radiation that can cause skin cancer or blindness, as well as negative affect in plant and animal life [Figure 3]. [6]

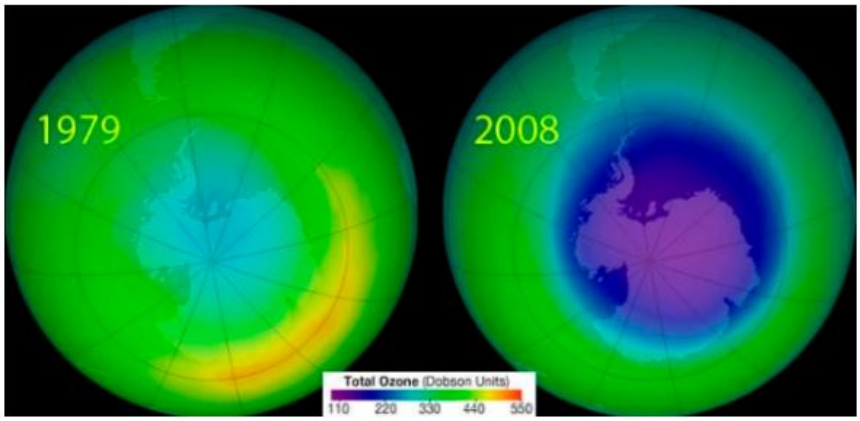


Figure 3- Evolution ozone layer 1979 vs 2008 [7]

In general, ozone (O_3) molecules are subjected to a continuous and uninterrupted process of destruction and regeneration, absorbing ultraviolet radiation in that process, reactions that take place are:

$$O_3 + UV \rightarrow O_2 + O$$

$$O + O_2 \rightarrow O_3$$

Although HCFCs and CFCs do not directly destroy the ozone layer, but they are involved in a lot of chemical reactions in this process.

When these compounds released into the atmosphere, they are not degraded and reach the stratosphere. It is in this place where they are irradiated by UV light and decompose rapidly to release chlorine atoms, which begin a chain of photochemical

reactions that interfere with stratospheric ozone, giving rise to a molecule of oxygen and a molecule of chlorine monoxide which ends up being a free radical, and the process can theoretically be repeated indefinitely. It doesn´t only removes one ozone molecule, but the destroyed oxygen atom prevents the regeneration of another ozone molecule [6] [8] [9]

It was estimated that a chlorine atom, before being neutralized, can destroy one hundred thousand ozone molecules. The Figure 4 shows the ozone depletion process in a simplified form.[9]

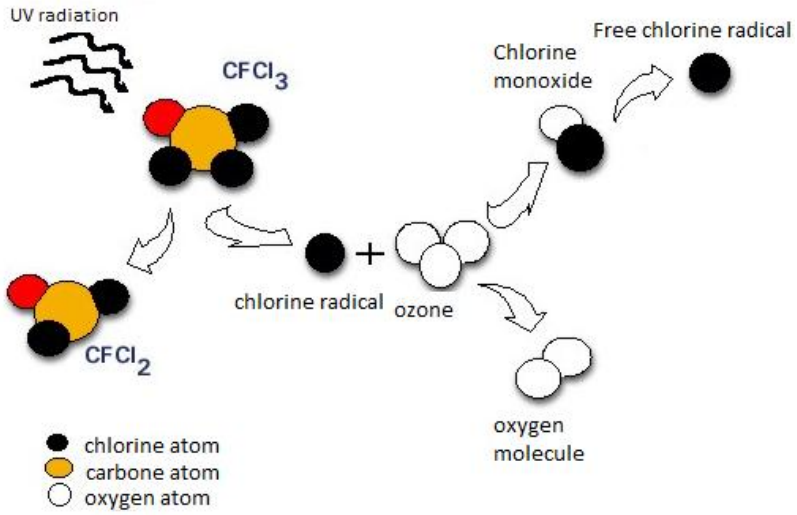


Figure 4- Ozone depletion [9]

In order to prevent this effect, hydrofluorocarbons (HFCs) began to be developed which, as they do not contain chlorine within their structure, do not contribute to the formation of the hole in the ozone layer.

These current generation refrigerants, known as "green" or "ecological", have zero ozone depletion potential; however, when released to the atmosphere, they have significant global warming potential (GWP), which are mainly responsible for the planet's climate change. In fact, these compounds have much higher global warming potentials than CO_2.[10] [11]

The increase in regulations and restrictions on the use of refrigerants based on CFCs, HCFCs and HFCs has meant that research into new generation of low-GWP refrigerants that are less harmful to the environment are in development. [12]

1.3 Refrigerants: rules and regulation

Due to the environmental problems described in the previous chapter a world level legislative provision was approved and published: **The Montreal protocol** has been designed to reduce the production and consumption of many substances, known as ODS (halons, carbon tetrachloride (CTC), CFCs, HCFCs, trichloroethane, methyl chloroform, methyl bromide (BM), methyl bromide and bromochloromethane (BCM), these substances react with ozone and are believed to be responsible for ozone depletion. This is a protocol that took place in the Vienna Convention for the protection of the Ozone Layer.

It also regulates trade, communication of monitoring data, research, information exchange and technical assistance to developing countries. And sets out the deadlines by which Parties must undertake to limit the levels of production and consumption of these substances. It was ratified by 197 countries and entered into force on 1 January 1989.

Since then, this document has been revised several times and it is believed that if all countries comply with the objectives proposed within the treaty, the ozone layer could have recovered by 2050. [13]

During the XXVIII Meeting of the Parties of The Montreal protocol (10-15 October 2016), **the Kigali amendment** was signed (into forced 1 January 2019) to reduce the use of HFCs worldwide. This agreement reinforced the objective of **the Paris Agreement** which aims to keep global warming below 1.5 °C to 2 °C by the year 2100.

The adoption of this amendment stems from the need to address the climate impact of the introduction of HFCs as the main substitutes for HCFCs, particularly in the refrigeration and air-conditioning sectors. Although these do not have an impact on the stratospheric ozone layer, some of them have a high GWP.

With its full implementation, it can prevent up to 0,4 °C of global warming by the end of this century while continuing to protect the ozone layer. The agreement provides that over the next 30 years the projected production and consumption of HFCs will be reduced by more than 80%. [14] [15]

About the global warming regulation **the Kyoto Protocol** is an international treaty, which represents one of the best examples of international commitment to global

environmental policies, that aims to reduce emissions of six greenhouse gases that cause global warming. These gases are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and the other three are types of fluorinated industrial gases: HFCs, perfluorocarbons (PFCs) and Sulphur hexafluoride (SF_6).

The protocol agreed on a reduction of at least 5% in emissions of these gases in 2008-2012 compared to 1990 emissions. This does not mean that each country committed itself to reduce its emissions of regulated gases by at least 5%, this is a percentage corresponding to a global commitment and each country subscribing to the protocol had its own emission reduction commitments. The protocol was adopted on 11 December 1997 in Kyoto (Japan) but did not enter into force until 16 February 2005. As of November 2009, 187 states had ratified it. The United States, when the protocol was signed, was the largest emitter of greenhouse gases (China has been since 2005), but never ratified it. [13]

In this regulation Italy was committed to reducing its greenhouse-gas emissions (GHGs), by 6,5% in the 2008-2012 period compared to the level of 1990. The Italian energy sector is characterized by very high costs of abatement of GHGs emissions because of the massive consumption of fossil fuels, the low energetic intensity and the dispersion of production activities.

The Higher Institute for Environmental Protection and Research (ISPRA) said that in the 2008-2012 period Italy reduced its greenhouse emissions by 4,6%. It said this means Italy is just the equivalent of 16,9 million tons of carbon dioxide away from meeting the target for this period. ISPRA said Italy's greenhouse emissions were down 5.4% in 2012 with respect to the previous year and 11.4% lower than in 1990, due to greater use of renewables to generate power and lower energy consumption due to the economic crisis. [16] [17]

Italy adopted, in 2016**, Law nº 79/2016**, “Ratification of the Doha amendment to the Kyoto Protocol”, which establishes, according to article 12 of 525/2013/EU, committed to develop, publish and regularly update national emission inventories of greenhouse gases formulate and implement programs to reduce these emissions, as a Part to the Convention and the Kyoto Protocol. [17]

Spain undertook to limit the increase in its emissions to a maximum of 15 % in relation to the base year. But according to the Fundation Alternatives Sustainability Spain Report in 2017, this country has increased its emissions by 15% in the last 27 years.

At European level **Regulation (EU) No 517/2014** of the European Parliament and of the Council (16 April 2014) on fluorinated greenhouse gases, reports obligations on hydrofluorocarbons following the Kigali Amendment to the Montreal Protocol. It has the object to protect the environment by reducing emissions of fluorinated gases from GHG. It lays rules on the containment, use, recovery and destruction of fluorinated gases from greenhouse effect, about conditions for the placing on the market of specific products and equipment containing fluorinated greenhouse gases or whose functioning relies on them and it sets conditions for specific uses of fluorinated greenhouse gases and the market of HFCs. [18]

The low carbon Roadmap (Brussels 2011) is a European regulation that sets out cost-efficient pathways for key economic sectors for achieving an overall 80% to 90% reduction in the EU's emissions by 2050 (compared to 1990). It shows that domestic emission cuts of the order of 40% and 60% below 1990 levels could be achieved (in a cost-effective way) by 2030 and 2040, respectively. Current policies are projected to reduce emissions domestically to -30% in 2030 and -40% in 2050. [19] [20]

1.4 Refrigerants evolution

The **first refrigerants** are natural refrigerants, used in the first mechanical cold production machines (1867). The most important natural refrigerant are: ammonia, carbon dioxide, sulphur dioxide, dimethylether and ethyl ether. However, these refrigerants presented great problems of toxicity (except ammonia) explosion and corrosion in the installations, so their use was restricted to industrial uses. [21] [22] [23]

In the 1930s, chlorofluorocarbon (CFC) refrigerants were introduced as safe alternatives to the chemicals used before them. The first fluid synthesized was R-12 (F_2CCl_2) and then other like R-11 ($FCCl_3$) and R-115 (F_2ClCCF_3). CFCs came to dominate first refrigeration and later HVAC (heating, ventilating and air conditioned) because of their safety and efficiency. Hydrochlorofluorocarbons fluids (HCFCs) such as R-22 (F2CClH), were added to this **second generation of refrigerant** alternatives in the 1950s. Only natural refrigerant survived: ammonia: due to its

excellent thermodynamic properties, it continued to be used, especially in Europe, in the applications of food preservation and brewery. [21] [22]

In the first years of this century the environmental emergency about anthropogenic global warming broke out. If released into the atmosphere, HCFCs and CFCs products are strong greenhouse gases and contribute to the disappearance of the ozone layer. This relative amount of degradation to the ozone layer is measure with the ozone depletion potential (ODP): high OPD equals high layer destruction.
Trying to finish with this situation forced the enactment of legislative provisions at world level with the Montreal protocol. Banning ozone-depleting substances and placing restrictions on greenhouse gases respectively.

The third generation of refrigerants was born. Its characteristics were focused in products somewhat like the previous ones but excluding the presence of chlorine in the molecule. They were HFC refrigerants (HydroFluoroCarbons). It doesn´t have destructive effect on ozone layer. Moreover, they have a shorter lifetime while maintaining its stability in the refrigeration circuit. The most frequently used refrigerant of this generation is R134a. [24]

However, in the 1990s, concerns grew up about the environmental emergency about anthropogenic global warming. With this problem a new concept was born: Global Warming Potential (GWP), it is a measure of how much heat a greenhouse gas traps in the atmosphere up to a specific time horizon, relative to carbon dioxide. It compares the amount of heat trapped by a certain mass of the gas in question to the amount of heat trapped by a similar mass of carbon dioxide and is expressed as a factor of carbon dioxide (whose GWP is standardized to 1). HFCs have a relatively high GWP, and this contributes to global warming when it is released to the atmosphere. [25]
This one forced the enactment of legislative provisions at world level: the Kyoto Protocol. Kyoto set reduction targets for greenhouse gases, including HFCs, in developed countries. [26]

With this new legislation **the fourth generation of refrigerants** was born. It does not affect the ozone layer at all, and its impact in terms of greenhouse gases is minimum. These gases are those based on hydrofluoro-olefins (HFO), the product of years of research and innovation that became the future of refrigerants.

Unfortunately, the number of suitable HFO compounds is rather limited, and the reactivity associated to the double bond makes most of them mildly flammable (with exceptions) so many of them are still under development.

The Figure 5 shows a sketch of the evolution of refrigerants in stages as a summary.

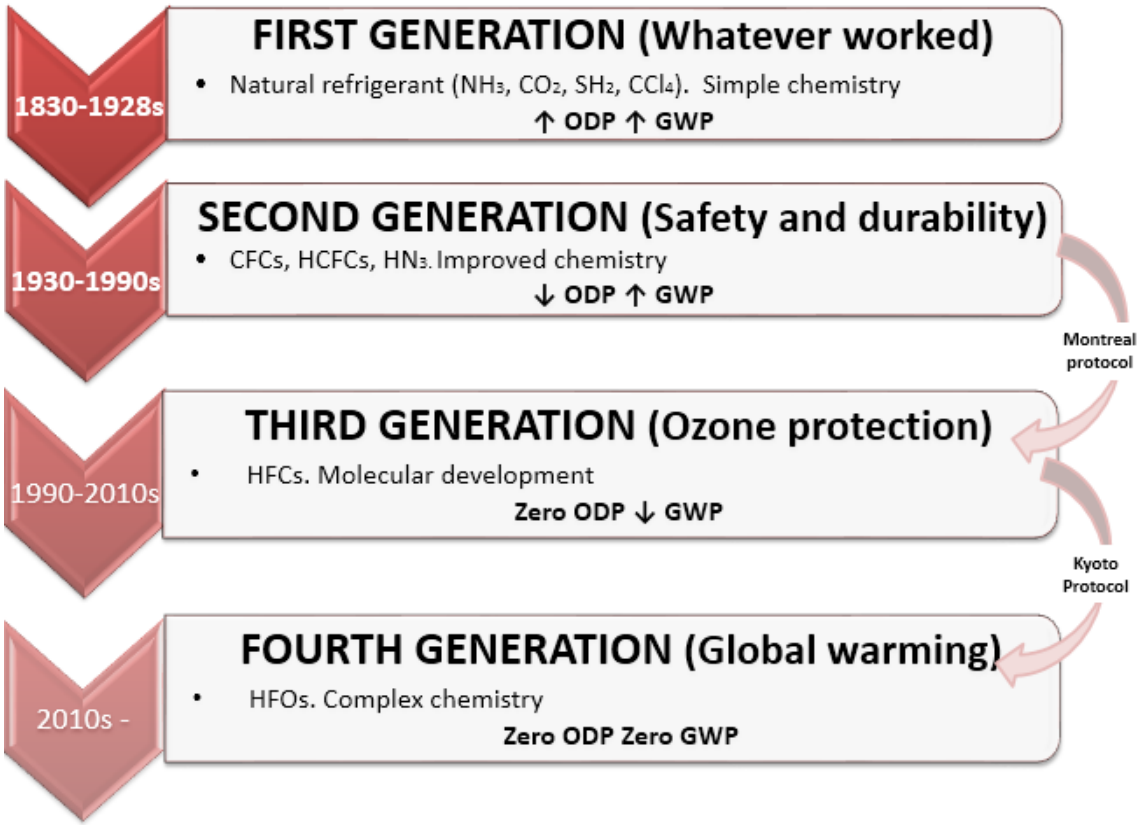


Figure 5- The evolution of refrigerants

1.5 Characteristics of refrigerants in heat pump

Nowadays any substance that can be considered as the ideal refrigerant. However, there are certain properties which a good refrigerant should have.

1.5.1 Desirables thermodynamic characteristic

- **Temperature**

There are three temperatures that are important for a refrigerant: boiling, critical and freezing temperatures. The boiling temperature of a refrigerant is always referred to the normal atmospheric pressure (101,3 kPa). In general, these

temperatures are fixed by the application but the refrigerant that has the lowest saturation pressures, although always higher than the atmospheric pressure, it is of interest in order to avoid the entry of air, as this facilitates the mechanical design of valves and pipes. The boiling point of a refrigerant must be low, so that even when operating at positive pressures, a low temperature can be reached in the evaporator.

In general, when the system is working, the boiling temperature of the liquid refrigerant inside the evaporator is approximately 5 °C lower than the evaporator temperature.
The evaporator must have a lower temperature than that desired in the refrigerated space, since a temperature difference is needed for the heat flow to exist.

For the condenser design is important to consider the critical temperature, because no steam condenses to a temperature higher than the critical, even if the pressure is very high. In the case of air-cooled condensers, it is desirable for the refrigerant to have a critical temperature greater than 55 °C. In Table 1 shows as all refrigerants have critical temperatures above 70 °C (with the exception of R-170, ethane, which is 32,3 °C therefore, this refrigerant cannot be used in air-cooled condensers, as the condensing temperature would always be higher than the critical temperature).
On the other hand, the freezing temperature of a refrigerant must be lower than the evaporator temperature. A refrigerant that freezes at the working temperature of the evaporator cannot be used. This is not a problem because most refrigerants have very low freezing temperatures, except for R-718 (water), which is never used in a compression refrigeration mechanism. [24] [27]

Table 1- Refrigerants temperatures [ºC] [27]

COMMUN REGRIGERANTS	BOILING TEMPERATURE	CRITICAL TEMPERATURE	FREEZING TEMPERATURE
R-12	-29,8	112	-158
R-22	-40,7	96	-160
R-30	40,6	216,1	-97
R-134a	-26,5	101,1	-103

R-123	27,9	163,3	-107
R-170	-88,6	32,3	-172
R-500	-45,4	82,2	-
R-717	-33,3	132,9	-78
R-718	100	374,5	0

- **Pressure**

The characteristic pressures in a refrigeration system are extremely important. On the one hand, it is necessary to operate with positive pressures (both in the condenser and in the evaporator, they must be higher than the atmospheric pressure). If the pressure in the evaporator is negative (works under vacuum), it exists a risk of leakage of air into the system. For this reason, the refrigerant must have the lowest possible evaporating pressure (but slightly higher than the atmospheric pressure).

On the other hand, the condensing pressure must be low enough, as this determines the compressor and condenser hard. If there is a high pressure, more work needs, and therefore more expensive equipment is required.

For example, the high condensing pressure is R-170, for which extremely hard equipment is required to withstand pressures above 4660 kPa. The refrigerants R-30 and R-123 would work under vacuum in the evaporator at this temperature. [Table 2]

The R-134a works at pressures closer to the ideal, since its evaporating pressure is very low, without reaching the vacuum, and its condensing pressure is not so high, so it does not require a very sturdy equipment. [24] [27]

Table 2- Pressure operation [kPa] [27]

COMMUN REGRIGERANTS	EVAPORATOR (-15 ºC)	CONDENSER (30 ºC)
R-12	183	754
R-22	296	1,192

R-30	8	69
R-134a	164	767
R-123	16	110
R-170	1627	4660
R-500	214	880
R-717	236	1,167
R-718	0,8	4,5

- **Enthalpy**

This property represents the total amount of thermal energy or heat content in a fluid. However, the important aspect for refrigerants is the change of enthalpy (evaporation enthalpy): the amount of heat required to heat or cool a kilogram of liquid, from one saturation temperature to another. This value is also known as "latent heat of evaporation".

In refrigeration systems, this change of state from liquid to vapor, it happens in the evaporator. The heat content or resulting enthalpy can be considered as the real work produced by a refrigerant within the refrigeration system. It is the absorbed heat as results in a useful cooling. It can be determined by knowing the enthalpy of the liquid refrigerant when it enters the evaporator, and the enthalpy of the refrigerant vapor exiting the evaporator. The difference between these two values is the actual work produced or "cooling effect". [27]

1.5.2 Desirables physics characteristic

- **Miscibility with lubricant oil.** The lubrication is necessary to reduce the friction and noise between the metal parts of the compressor. They must be a perfect mixture between the refrigerant and the lubricant, with this mixture the refrigerant is not deposited anywhere in the installation. Otherwise, an oil separator should be installed at the compressor discharge [27]

- **Tendency to run away** All refrigerants tend to leak, and when this happens, it should be easily detectable. There are different factors that determine the tendency of refrigerants to leak: pressure, viscosity, density, scent...

Moreover, the refrigerants that have the most tendency to leak are the ones with the lowest molecular weight.

The Table 3 shows some different factors. It can be observed that ammonia has a molecule about half size of R-22. This means that, under equal conditions, it needs a crack twice the size for R-22 leaks as R-717. For the ease with which the ammonia leaks in refrigeration facilities, it has usually that it has a very common and recognizable odor.

A little smell in refrigerants can be an advantage, as any leak (however small) could be noticed immediately and corrected before all the refrigerant is lost. Although a strong, pungent odor, such as ammonia, helps indicate a leak, it can also cause panic by creating more important problems than simply losing refrigerant. Therefore, although a slight odor may be advantageous, an odorless refrigerant will usually be better than an extremely offensive odor. However, the refrigerants that are odorless and very toxic, such as R-170, sometimes an irritating odor is added to these compounds as a precautionary measure.

Table 3- Molecular weights [g/mol] and characteristic odor of some refrigerants [27]

COMMUN REGRIGERANTS	SCENT	MOLECULAR WEIGHT
R-12	Slightly	120,93
R-22	Slightly	86,48
R-30	Sweet	85,00
R-134a	Slightly	102,03
R-123	Slightly	152,95
R-170	Sweet	30,05
R-500	Slightly	99,31
R-717	Spicy	17,03
R-718	Odourless	18,02

1.5.3 Desirables security characteristic

The safety properties of a refrigerant are analyzed in two ways: toxicity and flammability. The ideal refrigerant should be non-flammable and non-toxic. However, this is not the case for many of these substances, especially for those currently considered alternatives to HFCs.

- **Toxicity**

The toxicity in refrigerants is governed by the maximum in toxicology which would say that they are only dangerous if certain concentrations in the air are exceeded. It is quantified through the ATEL limit. The acute toxicity exposure limit (LETA/ATEL) is defined as the maximum recommended concentration of refrigerant intended to reduce the risk of acute toxicity to humans in the event of refrigerant leakage or release. This factor contemplates the different degrees of toxicity, from the anaesthetic effect to mortality, including cardiac toxicity (difficulty of the heart to pump enough blood), among others. If one fluid is toxic, by leaking it can intoxicate people or contaminate food. [28] [29]

The ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) has divided refrigerants into two groups according to their toxicity

- Class A: Low or no toxicity, that is, with concentrations of less than or equal to four-hundred parts per million there are no signs of toxicity. In case of leakage, people are not intoxicated. Some example refrigerants that are rated as nontoxic are R-22, R-134a, or R-410A.
- Class B: Toxic. They present intoxication signs in people at concentrations lower than 400 ppm. They require specific extraction systems and specific conditions of use. They cannot be in direct contact with food. An example refrigerant is Ammonia (R-717). [27]

- **Flammability**

The concentration limits in the air, where ignition or explosion is possible, also indicate the degree of safety of the refrigerant. In order to detect these limits, a test is carried out by bringing an ignition source closer to a mixture of refrigerant in gas and air, at a certain pressure and temperature. [Figure 6] [28]

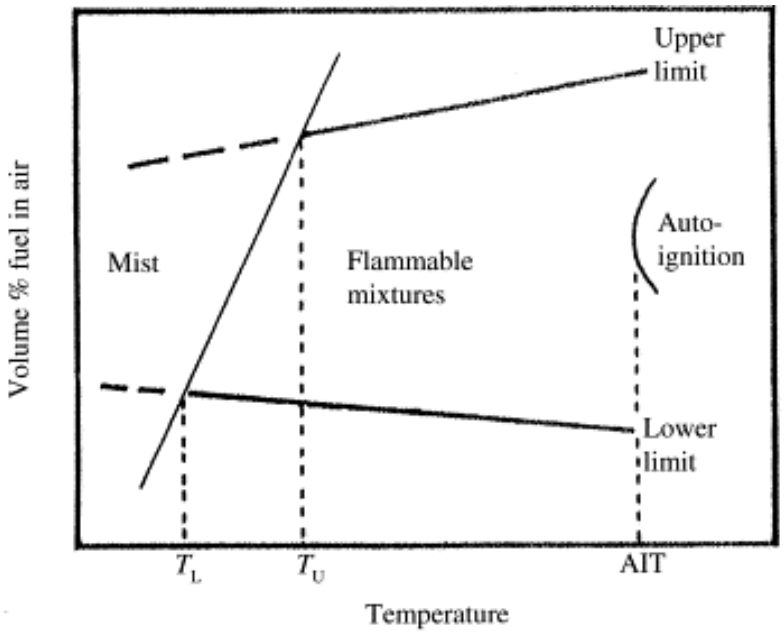


Figure 6- Flammability relation [28]

In this way, three categories of refrigerants can be:

- Category 1: no flame. At 101 KPa pressure and 21 ºC temperature, there is no combustion.
- Category 2: at 101 KPa pressure and 21 ºC temperature, there is a small flame propagation. The heat produced by combustion is less than 19000 KJ/Kg. The concentration of refrigerant fluid is less than 0,15 l/Kg Air.
- Category 3: highly flammable. At 101 KPa of pressure and 21 ºC of temperature a great combustion takes place. The heat produced is greater than 19000 KJ/Kg. The concentration of refrigerant fluid is less than 0,15 l/Kg Air.

The Table 4 shows examples of safety classification of some refrigerants

Table 4- Safety classification of some refrigerants [28]

COMMUN REGRIGERANTS	SAFETY CLASSIFICATION
R-12	A1
R-22	A1
R-30	B2
R-134a	A1
R-123	B1
R-170	A1
R-500	B2
R-717	A2

This thesis is going to be focus in the evaluation of different eco-friendly refrigerants, with low GWP and no ODP, for heat pump and their risk assessment.

2 Low GWP alternative refrigerant in heat pumps

Nowadays, there is no perfect low global warming potential refrigerant to replace HFCs in refrigeration and air-conditioning systems, as there are some relevant disadvantages to each alternative. Therefore, in order to replace HFCs, a refrigerant must be selected as a compromise solution between different parameters considering the characteristics of each application (environmental, economic, efficiency...).[31]

In the use of heat pumps for high water temperature applications highlights CO_2. It usually used transcritical cycle. It is a thermodynamic cycle where the working fluid goes through both subcritical and supercritical states. It is cool but does not condense at the gas cooler outlet, being above critical temperature as Figure 7 shows.

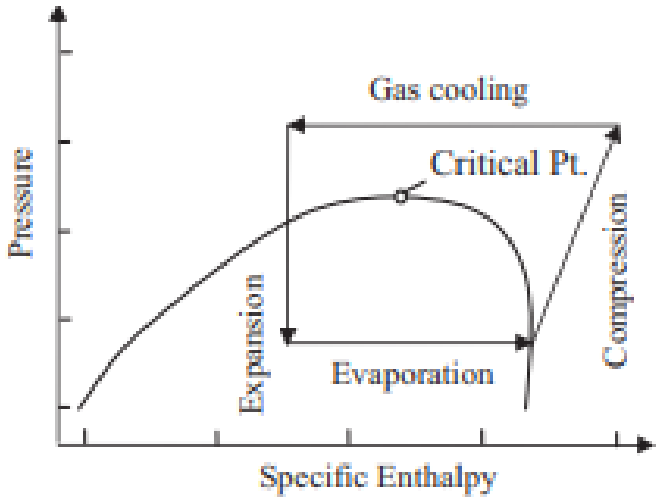


Figure 7 p-h transcritical cycle [32]

Hydrocarbons as HC-600a and HC-290 are suitable for heat pumps with low capacities of below 20 kW. Industrial heat pumps can be based on HC-600a or ammonia. [34]

R-404A, R-407C and R-410A are HFC blends and they are the most dominant refrigerants in heat pump application. Out of them, R-410A is one of the main refrigerants used for heat pump systems in residential applications. R-410A is a near-azeotropic mixture, blend of HFC-125(C_2HF_5) and HFC-32 (CH_2F_2)). It has zero ODP, not flammable and not toxic.
Although R-410A has good thermal and transport properties and high volumetric capacity and A1 safety group it has relatively high GWP (2088 times greater than that of CO_2). Its use is restricted by the legislation described above and the search for its replacement is in progress. [34] [35]

2.1 Alternative refrigerants to R-410A

A few synthetic refrigerants proposed as the replacements for R-410A with some of the candidates are still in the development stage. Some of them are R-32, R-1234yf, R-1234ze(E)… All these refrigerants are suitable for drop-in. Other low GWP refrigerants, like CO_2 and ammonia, are also possible R-410A replacements, however it will be necessary an intensive re-design. [35]

- **R-32** is a pure refrigerant which is suitable for heat pump applications. It has zero ODP and offers significant GWP reduction (677, and R-410A GWP is 1924). It classified as low flammable (A2L). R-32 has higher volumetric capacity than R-410A what leads to reduced refrigerant charge whist maintaining similar system performance. [34] [35]

In the HFO refrigerant family highlight as a replacement for R-410A:

- **R-1234yf** has very low GWP and zero ODP. But it has high flammability, so it has a very high risk, with strong limitations in applicability.
  Moreover since 2018, all new cars weighing less than 3,5 tonnes have been fitted by law with an air-conditioning system using this fluorinated gas, it was the replacement of refrigerant R134a.

- **R-1234ze(E)** is required a larger unit to achieve similar performance that R-410A because its lower vapor density and latent heat. It is slightly flammable and requires small changes in equipment design for use in new equipment. In safety data sheets, R1234ze(E) is declared as non-flammable. However, this is only to transport and storage. When used as a refrigerant, a higher reference temperature of 60 °C for flammability tests is valid. At this temperature, R1234ze(E) is flammable and therefore classified in the same safety group A2L as R1234yf.

- Another low-GWP alternatives refrigerants for R-410A is **R-446a (L41a)**. That is ternary mixture of R32, R1234yf and R1234ze (73/15/12% by mass). It is environmentally friendly due to its low GWP, 461 and belongs to A2L safety group. [35]

- **R-454b** is a mildly flammable and low GWP (78% less that R-410A) and ensures better performance. It is mixture of R32 and R1234yf (83% and 17% by molar mass) It offers similar properties to the R-410A, making it easy and convenient to apply without requiring significant changes.[36]

- **R-452b** is a non azeotropic mixture, it has the same substances as r-410A but with a 26% increase in R1234yf. R32: 69% and R125: 31%. Its GWP is 67% lower than R-410A for low temperature applications

An example of the heating cycle, t vs s diagram, can show in the Figure 8, in this one was used as refrigerants R1234yf. This one is calculated for a condenser temperature of 0 ºC and an evaporator temperature of 45 ºC.

To graph this cycle, the saturation line (blue line of Figure 8) for the conditions described must know. For this purpose, the corresponding saturation vapor and liquid entropies are calculated in the temperature range of 0°C, arbitrarily chosen, to the critical temperature. The R1234yf critical temperature is calculated used the REPFROP program and it has a value of 94,7 ºC. The Table 5 shows the saturation values for R1234yf fluid.

Table 5- Saturation values of R1234yf

Temperature (K)	Entropy CLI	Entropy CLS	Temperature (K)	Entropy CLI	Entropy CLS
273,15	1,0000	1,5978	320,65	1,2197	1,6089
273,65	1,0023	1,5979	321,15	1,2220	1,6089
274,15	1,0047	1,5980	321,65	1,2243	1,6090
274,65	1,0070	1,5981	322,15	1,2266	1,6091
275,15	1,0094	1,5981	322,65	1,2289	1,6091
275,65	1,0117	1,5982	323,15	1,2312	1,6092
276,15	1,0141	1,5983	323,65	1,2336	1,6092
276,65	1,0164	1,5984	324,15	1,2359	1,6093
277,15	1,0187	1,5985	325,15	1,2405	1,6094
277,65	1,0211	1,5986	325,65	1,2428	1,6094
278,15	1,0234	1,5987	326,15	1,2452	1,6094
278,65	1,0258	1,5988	326,65	1,2475	1,6095
279,15	1,0281	1,5989	327,15	1,2498	1,6095
279,65	1,0304	1,5990	327,65	1,2522	1,6095
280,15	1,0328	1,5991	328,15	1,2545	1,6095
280,65	1,0351	1,5992	328,65	1,2568	1,6095
281,15	1,0374	1,5993	329,15	1,2592	1,6095

281,65	1,0397	1,5995
282,15	1,0421	1,5996
282,65	1,0444	1,5997
283,15	1,0467	1,5998
283,65	1,0491	1,5999
284,15	1,0514	1,6000
284,65	1,0537	1,6002
285,15	1,0560	1,6003
285,65	1,0584	1,6004
286,15	1,0607	1,6005
286,65	1,0630	1,6007
287,15	1,0653	1,6008
287,65	1,0676	1,6009
288,15	1,0699	1,6010
288,65	1,0723	1,6012
289,15	1,0746	1,6013
289,65	1,0769	1,6014
290,15	1,0792	1,6016
290,65	1,0815	1,6017
291,15	1,0838	1,6018
291,65	1,0862	1,6020
292,15	1,0885	1,6021
292,65	1,0908	1,6022
293,15	1,0931	1,6024
293,65	1,0954	1,6025
294,15	1,0977	1,6026
294,65	1,1000	1,6028
295,15	1,1023	1,6029
295,65	1,1046	1,6030
296,15	1,1069	1,6032
296,65	1,1092	1,6033
297,15	1,1115	1,6034
297,65	1,1139	1,6036

329,65	1,2615	1,6095
330,15	1,2638	1,6095
330,65	1,2662	1,6095
331,15	1,2685	1,6095
331,65	1,2709	1,6094
332,15	1,2732	1,6094
332,65	1,2756	1,6094
333,15	1,2779	1,6093
333,65	1,2803	1,6093
334,15	1,2827	1,6092
334,65	1,2850	1,6092
335,15	1,2874	1,6091
335,65	1,2898	1,6090
336,15	1,2922	1,6089
336,65	1,2946	1,6088
337,15	1,2969	1,6087
337,65	1,2993	1,6086
338,15	1,3017	1,6085
338,65	1,3041	1,6084
339,15	1,3065	1,6082
339,65	1,3090	1,6081
340,15	1,3114	1,6079
340,65	1,3138	1,6078
341,15	1,3162	1,6076
341,65	1,3187	1,6074
342,15	1,3211	1,6072
342,65	1,3235	1,6070
343,15	1,3260	1,6068
343,65	1,3285	1,6065
344,15	1,3309	1,6063
344,65	1,3334	1,6060
345,15	1,3359	1,6058
345,65	1,3384	1,6055

298,15	1,1162	1,6037
298,65	1,1185	1,6039
299,15	1,1208	1,6040
299,65	1,1231	1,6041
300,15	1,1254	1,6043
300,65	1,1277	1,6044
301,15	1,1300	1,6045
301,65	1,1323	1,6047
302,15	1,1346	1,6048
302,65	1,1369	1,6049
303,15	1,1392	1,6051
303,65	1,1415	1,6052
304,15	1,1438	1,6053
304,65	1,1461	1,6055
305,15	1,1484	1,6056
305,65	1,1507	1,6057
306,15	1,1530	1,6059
306,65	1,1553	1,6060
307,15	1,1576	1,6061
307,65	1,1599	1,6062
308,15	1,1622	1,6064
308,65	1,1645	1,6065
309,15	1,1668	1,6066
309,65	1,1691	1,6067
310,15	1,1714	1,6068
310,65	1,1737	1,6070
311,15	1,1759	1,6071
311,65	1,1782	1,6072
312,15	1,1805	1,6073
312,65	1,1828	1,6074
313,15	1,1851	1,6075
313,65	1,1874	1,6076
314,15	1,1897	1,6077

346,15	1,3409	1,6052
346,65	1,3434	1,6048
347,15	1,3459	1,6045
347,65	1,3484	1,6042
348,15	1,3510	1,6038
348,65	1,3535	1,6034
349,15	1,3561	1,6030
349,65	1,3586	1,6026
350,15	1,3612	1,6021
350,65	1,3638	1,6016
351,15	1,3664	1,6011
351,65	1,3691	1,6006
352,15	1,3717	1,6001
352,65	1,3743	1,5995
353,15	1,3770	1,5989
353,65	1,3797	1,5983
354,15	1,3824	1,5976
354,65	1,3851	1,5969
355,15	1,3879	1,5962
355,65	1,3907	1,5954
356,15	1,3934	1,5946
356,65	1,3963	1,5937
357,15	1,3991	1,5928
357,65	1,4020	1,5919
358,15	1,4049	1,5909
358,65	1,4079	1,5898
359,15	1,4109	1,5886
359,65	1,4139	1,5874
360,15	1,4170	1,5862
360,65	1,4201	1,5848
361,15	1,4234	1,5833
361,65	1,4266	1,5817
362,15	1,4300	1,5800

314,65	1,1920	1,6078	362,65	1,4334	1,5782
315,15	1,1943	1,6079	363,15	1,4370	1,5762
315,65	1,1966	1,6080	363,65	1,4407	1,5740
316,15	1,1989	1,6081	364,15	1,4446	1,5715
316,65	1,2012	1,6082	364,65	1,4486	1,5688
317,15	1,2035	1,6083	365,15	1,4529	1,5657
317,65	1,2059	1,6084	365,65	1,4575	1,5621
318,15	1,2082	1,6085	366,15	1,4626	1,5578
318,65	1,2105	1,6086	366,65	1,4685	1,5524
319,15	1,2128	1,6087	367,15	1,4759	1,5451
319,65	1,2151	1,6087	367,65	1,4879	1,5318
320,15	1,2174	1,6088	367,85	1,5087	1,5087

The R1234yf cycle is in the Figure 8 (red line) has been created with a similar excel sheet used to calculate the COP. Calculating enthalpies corresponding to the four elements of the heat pump explained in the introduction. Getting to know, for example, that the evaporator outlet and compressor inlet are saturated vapor. And the output of the condenser is saturated liquid. Moreover, the water used in the condenser is appeared too as the brown line.

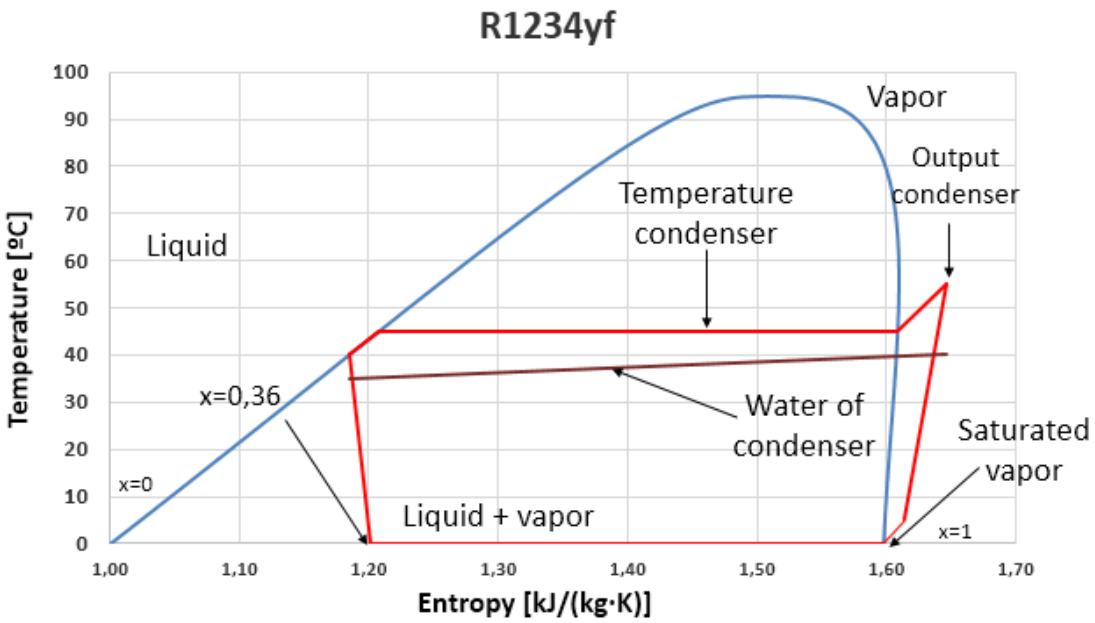


Figure 8- T vs s diagram for R1234yf refrigerant

2.1.1 Analysis of the capacity of the different alternatives

The measure COP is used to compare the different refrigerants explained above. The COP is calculated as the ratio of the heat flux, which is exchanged in the condenser between the refrigerant and the fluid used for transporting the heat, and the power output at the compressor accounting for the refrigerant vapor compression (regardless of the electricity used by the pump or fans). The COP expression is:

$$COP_{max} = {}^{Q_{con}}/_{W}$$

The condenser heat flux (Q_{con}) was calculated as the different between the enthalpy (hi) in the condenser and the superheated vapor enthalpy at the condenser input:

$$Q_{con} = h_{cond.out} - h_{comp.out.real}$$

And the power used (W) for a compression of refrigerant vapor was calculated as the different between the superheated vapor enthalpy at the compressor output and the superheated vapor enthalpy at the compressor input divided by electrical efficiency of the compressor, using a standard electrical efficiency of 0,70:

$$W = {}^{(h_{comp.in} - h_{comp.out.real})}/_{\eta_{electrical}}$$

These calculations have been made using an excel spreadsheet. It considers the refrigerant, the condenser temperature according to the application, the pressure in the evaporator. With these data, the enthalpy and entropy(s_i) are calculated as state functions:

$$h_{cond.out} = f(T_{out\ cooler\ gas,} P_{gas\ cooler});$$

$$T_{out\ cooler\ gas}[°C] = T_{condeser} - 10 \text{ and } P_{gas\ cooler} \text{ is supposed a value of 98 bar.}$$

$$s_{comp.int} = f(T_{comp,} P_{evap})$$

$$h_{comp.in} = f(T_{comp,} P_{evap})$$

$$h_{comp.out.teor} = f(s_{comp.int}, P_{gas\ cooler})$$

$h_{comp.out.real} = h_{comp.in} + \frac{h_{comp.out.teor} - h_{comp.in}}{\eta_{isoentrop}}$; $\eta_{electrical}$ is supossed a standard value of 0,89

The COP is going to calculate for three different heating applications:

- Radiators: they are one of the main heating systems using in home in the world. They emitter and dispense the heat that comes from the water that runs inside them. The required condensation temperature is 70 ºC.
- Radiant floor: consists of the emission of heat by the water circulating through pipes in a concrete slab that forms the floor, achieving a large surface area as a heat emitting element. In winter, the condensation temperature is between 30-40 ºC.
- Fan coil (or Vertical Fan Coil-Unit): is a device consisting of a heating and/or cooling heat exchanger and fan. This system can find in residential, commercial, and industrial buildings. It needs 45 ºC in the condenser.

The geothermal temperature has been taken from 18-20 ºC. Moreover, to avoid breakage of the compressor, the compressor temperature was assumed to be 5 degrees lower than the geothermal temperature, 12 ºC.

The next tables [Table 6,Table 7,Table 8,Table 9,Table 10,Table 11,Table 12,Table 13,Table 14,Table 15,Table 16,Table 17,Table 18,Table 19,Table 20,Table 21,Table 22 and Table 23] show the thermodynamic aspects of fluids except for R-446a because no database has been found to have them.

These thermodynamic parameters are calculated for the above uses, i.e. different condensing temperatures and in a range of evaporator temperatures between -15 and 12 degrees are estimated the COPs.

Table 6- Thermodynamic parameters for radiator application, with a condenser temperature of 70 ºC and an evaporator temperature of -15 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	4,82	4,88	1,20	1,84	4,33	4,22
Temperature inlet compressor [ºC]	-10,00					
Condenser output enthalpy [kJ/kg]	295,0	332,9	292,5	293,4	319,4	319,5

Compressor inlet enthalpy [kJ/kg]	422,25	518,01	380,10	359,79	465,04	468,15
Compressor output theory enthalpy [kJ/kg]	512,93	622,64	427,22	400,83	551,72	548,48
Compressor output real enthalpy [kJ/kg]	552,32	667,91	448,34	419,30	589,47	583,45
Compressor inlet entropy [kJ/(kg·K)]	1,86	2,23	1,69	1,61	2,04	2,03
COP	1,7	2,0	2,0	1,8	1,9	2,0

Table 7- Thermodynamic parameters for radiator application, with a condenser temperature of 70 ºC and an evaporator temperature of -7 ºC

	R410A	**R32**	**R1234ze**	**R1234yf**	**R452b**	**R454b**
Evaporator pressure [bar]	6,37	6,46	1,66	2,47	5,72	5,58
Temperature inlet compressor [ºC]	-2,00					
Condenser output enthalpy [kJ/kg]	295,0	332,9	292,5	293,4	319,4	319,5
Compressor inlet enthalpy [kJ/kg]	424,21	519,54	383,67	363,20	467,27	470,16
Compressor output theory enthalpy [kJ/kg]	506,00	610,22	426,86	400,94	543,64	540,44
Compressor output real enthalpy [kJ/kg]	541,05	649,08	445,37	417,12	576,37	570,56
Compressor inlet entropy [kJ/(kg·K)]	1,84	2,20	1,69	1,61	2,01	2,01
COP	1,9	2,2	2,2	2,0	2,1	2,2

Table 8- Thermodynamic parameters for radiator application, with a condenser temperature of 70 ºC and an evaporator temperature of -2 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	7,51	7,62	2,01	2,95	6,75	6,59
Temperature inlet compressor [ºC]	3,00					
Condenser output enthalpy [kJ/kg]	295,0	332,9	292,5	293,4	319,4	319,5
Compressor inlet enthalpy [kJ/kg]	426,05	520,88	387,20	366,58	469,37	472,02
Compressor output theory enthalpy [kJ/kg]	501,90	602,88	426,79	401,16	538,90	535,71
Compressor output real enthalpy [kJ/kg]	534,41	638,02	443,76	415,97	568,70	563,00
Compressor inlet entropy [kJ/(kg·K)]	1,83	2,18	1,69	1,61	2,00	2,00
COP	2,0	2,3	2,4	2,2	2,2	2,4

Table 9- Thermodynamic parameters for radiator application, with a condenser temperature of 70 ºC and an evaporator temperature of 0 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	8,01	8,13	2,17	3,16	7,20	7,03
Temperature inlet compressor [ºC]	5,00					
Condenser output enthalpy [kJ/kg]	295,0	332,9	292,5	293,4	319,4	319,5
Compressor inlet enthalpy [kJ/kg]	426,75	521,37	388,61	367,93	470,17	472,73
Compressor output theory enthalpy [kJ/kg]	500,30	600,02	426,80	401,27	537,06	533,87
Compressor output real enthalpy [kJ/kg]	531,83	633,73	443,16	415,56	565,72	560,07

Compressor inlet entropy [kJ/(kg·K)]	1,83	2,18	1,69	1,61	2,00	1,99
COP	2,0	2,4	2,5	2,3	2,3	2,5

Table 10-Thermodynamic parameters for radiator application, with a condenser temperature of 70 ºC and an evaporator temperature of 7 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	9,95	10,12	2,78	3,98	8,95	8,74
Temperature inlet compressor [ºC]	12,00					
Condenser output enthalpy [kJ/kg]	295,0	332,9	292,5	293,4	319,4	319,5
Compressor inlet enthalpy [kJ/kg]	428,98	522,79	393,48	372,59	472,79	474,98
Compressor output theory enthalpy [kJ/kg]	494,84	590,32	426,93	401,76	530,83	527,62
Compressor output real enthalpy [kJ/kg]	523,07	619,26	441,26	414,27	555,71	550,19
Compressor inlet entropy [kJ/(kg·K)]	1,82	2,15	1,69	1,62	1,98	1,98
COP	2,2	2,6	2,8	2,6	2,5	2,7

Table 11-Thermodynamic parameters for radiator application, with a condenser temperature of 70 ºC and an evaporator temperature of 12 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	11,54	11,74	3,30	4,66	10,39	10,13
Temperature inlet compressor [ºC]	17,00					
Condenser output enthalpy [kJ/kg]	430,36	523,52	396,92	375,87	474,46	476,37
Compressor inlet enthalpy [kJ/kg]	1,81	583,62	427,13	402,2	526,55	523,31

Compressor output theory enthalpy [kJ/kg]	491,03	583,62	427,13	402,20	526,55	523,31
Compressor output real enthalpy [kJ/kg]	517,02	609,37	440,07	413,49	548,87	543,43
Compressor inlet entropy [kJ/(kg·K)]	1,81	2,13	1,69	1,62	1,97	1,96
COP	2,3	2,9	3,0	2,8	2,7	3,0

Table 12- Thermodynamic parameters for radiant floor application, with a condenser temperature of 35 ºC and an evaporator temperature of -15 ºC

	R410A	**R32**	**R1234ze**	**R1234yf**	**R452b**	**R454b**
Evaporator pressure [bar]	4,82	4,88	1,20	1,84	4,33	4,22
Temperature inlet compressor [ºC]	-10,00					
Condenser output enthalpy [kJ/kg]	238,0	255,2	240,8	240,5	250,2	250,4
Compressor inlet enthalpy [kJ/kg]	421,01	517,01	377,95	357,74	463,65	466,89
Compressor output theory enthalpy [kJ/kg]	512,93	581,61	410,63	386,68	520,87	518,34
Compressor output real enthalpy [kJ/kg]	552,32	609,29	424,64	399,09	545,39	540,39
Compressor inlet entropy [kJ/(kg·K)]	1,86	2,23	1,69	1,61	2,04	2,03
COP	2,1	3,4	3,5	3,4	3,2	3,5

Table 13- Thermodynamic parameters for radiant floor application, with a condenser temperature of 35 ºC and an evaporator temperature of -7 ºC

	R410A	**R32**	**R1234ze**	**R1234yf**	**R452b**	**R454b**
Evaporator pressure [bar]	6,37	6,46	1,66	2,47	5,72	5,58
Temperature inlet compressor [ºC]	-2,00					

Condenser output enthalpy [kJ/kg]	238,0	255,2	240,8	240,5	250,2	250,4
Compressor inlet enthalpy [kJ/kg]	424,21	519,54	383,67	363,20	467,27	470,16
Compressor output theory enthalpy [kJ/kg]	506,00	570,98	410,30	386,79	513,80	511,33
Compressor output real enthalpy [kJ/kg]	541,05	593,02	421,72	396,90	533,74	528,98
Compressor inlet entropy [kJ/(kg·K)]	1,84	2,20	1,69	1,61	2,01	2,01
COP	2,3	4,1	4,2	4,1	3,8	4,2

Table 14-Thermodynamic parameters for radiant floor application, with a condenser temperature of 35 ºC and an evaporator temperature of -2 ºC

	R410A	**R32**	**R1234ze**	**R1234yf**	**R452b**	**R454b**
Evaporator pressure [bar]	7,51	7,62	2,01	2,95	6,75	6,59
Temperature inlet compressor [ºC]	3,00					
Condenser output enthalpy [kJ/kg]	238,0	255,2	240,8	240,5	250,2	250,4
Compressor inlet enthalpy [kJ/kg]	426,05	520,88	387,20	366,58	469,37	472,02
Compressor output theory enthalpy [kJ/kg]	501,90	564,72	410,24	386,98	509,66	507,22
Compressor output real enthalpy [kJ/kg]	534,41	583,50	420,12	395,72	526,93	522,30
Compressor inlet entropy [kJ/(kg·K)]	1,83	2,18	1,69	1,61	2,00	2,00
COP	2,4	4,7	4,8	4,7	4,3	4,8

Table 15-Thermodynamic parameters for radiant floor application, with a condenser temperature of 35 ºC and an evaporator temperature of 0 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	8,01	8,13	2,17	3,16	7,20	7,03
Temperature inlet compressor [ºC]	5,00					
Condenser output enthalpy [kJ/kg]	238,0	255,2	240,8	240,5	250,2	250,4
Compressor inlet enthalpy [kJ/kg]	426,75	521,37	388,61	367,93	470,17	472,73
Compressor output theory enthalpy [kJ/kg]	500,30	562,28	410,25	387,08	508,06	505,62
Compressor output real enthalpy [kJ/kg]	531,83	579,82	419,52	395,29	524,30	519,71
Compressor inlet entropy [kJ/(kg·K)]	1,83	2,18	1,69	1,61	2,00	1,99
COP	2,5	4,9	5,1	5,0	4,5	5,1

Table 16- Thermodynamic parameters for radiant floor application, with a condenser temperature of 35 ºC and an evaporator temperature of 7 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	9,95	10,12	2,78	3,98	8,95	8,74
Temperature inlet compressor [ºC]	12,00					
Condenser output enthalpy [kJ/kg]	238,0	255,2	240,8	240,5	250,2	250,4
Compressor inlet enthalpy [kJ/kg]	428,98	522,79	393,48	372,59	472,79	474,98
Compressor output theory enthalpy [kJ/kg]	494,84	554,03	410,37	387,53	502,64	500,20
Compressor output real enthalpy [kJ/kg]	523,07	567,41	417,61	393,93	515,43	511,00

Compressor inlet entropy [kJ/(kg·K)]	1,82	2,15	1,69	1,62	1,98	1,98
COP	2,7	6,2	6,5	6,4	5,5	6,4

Table 17- Thermodynamic parameters for radiant floor application, with a condenser temperature of 35 ºC and an evaporator temperature of 12 ºC

	R410A	**R32**	**R1234ze**	**R1234yf**	**R452b**	**R454b**
Evaporator pressure [bar]	11,54	11,74	3,30	4,66	10,39	10,13
Temperature inlet compressor [ºC]	17,00					
Condenser output enthalpy [kJ/kg]	238,0	255,2	240,8	240,5	250,2	250,4
Compressor inlet enthalpy [kJ/kg]	430,36	523,52	396,92	375,87	474,46	476,37
Compressor output theory enthalpy [kJ/kg]	491,03	548,33	410,55	387,92	498,92	496,46
Compressor output real enthalpy [kJ/kg]	517,02	558,97	416,39	393,09	509,40	505,07
Compressor inlet entropy [kJ/(kg·K)]	1,81	2,13	1,69	1,62	1,97	1,96
COP	2,9	7,6	8,0	7,9	6,6	7,9

Table 18- Thermodynamic parameters for fan coil application, with a condenser temperature of 45 ºC and an evaporator temperature of -15 ºC

	R410A	**R32**	**R1234ze**	**R1234yf**	**R452b**	**R454b**
Evaporator pressure [bar]	4,82	4,88	1,20	1,84	4,33	4,22
Temperature inlet compressor [ºC]	-10,00					
Condenser output enthalpy [kJ/kg]	253,5	275,3	255,0	254,9	268,3	268,6
Compressor inlet enthalpy [kJ/kg]	421,01	517,01	377,95	357,74	463,65	466,89

Compressor output theory enthalpy [kJ/kg]	512,93	593,62	415,87	391,21	530,14	527,40
Compressor output real enthalpy [kJ/kg]	552,32	626,46	432,12	405,56	558,63	553,34
Compressor inlet entropy [kJ/(kg·K)]	1,86	2,23	1,69	1,61	2,04	2,03
COP	2,0	2,9	2,9	2,8	2,7	2,9

Table 19-Thermodynamic parameters for fan coil application, with a condenser temperature of 45 ºC and an evaporator temperature of -7 ºC

	R410A	**R32**	**R1234ze**	**R1234yf**	**R452b**	**R454b**
Evaporator pressure [bar]	6,37	6,46	1,66	2,47	5,72	5,58
Temperature inlet compressor [ºC]	-2,00					
Condenser output enthalpy [kJ/kg]	253,5	275,3	255,0	254,9	268,3	268,6
Compressor inlet enthalpy [kJ/kg]	424,21	519,54	383,67	363,20	467,27	470,16
Compressor output theory enthalpy [kJ/kg]	506,00	582,47	415,53	391,32	522,77	520,10
Compressor output real enthalpy [kJ/kg]	541,05	609,44	429,19	403,37	546,56	541,50
Compressor inlet entropy [kJ/(kg·K)]	1,84	2,20	1,69	1,61	2,01	2,01
COP	2,2	3,3	3,4	3,3	3,1	3,4

Table 20- Thermodynamic parameters for fan coil application, with a condenser temperature of 45 ºC and an evaporator temperature of -2 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	7,51	7,62	2,01	2,95	6,75	6,59
Temperature inlet compressor [ºC]	3,00					
Condenser output enthalpy [kJ/kg]	253,5	275,3	255,0	254,9	268,3	268,6
Compressor inlet enthalpy [kJ/kg]	426,05	520,88	387,20	366,58	469,37	472,02
Compressor output theory enthalpy [kJ/kg]	501,90	575,90	415,47	391,52	518,46	515,80
Compressor output real enthalpy [kJ/kg]	534,41	599,48	427,58	402,20	539,49	534,56
Compressor inlet entropy [kJ/(kg·K)]	1,83	2,18	1,69	1,61	2,00	2,00
COP	2,3	3,7	3,8	3,7	3,4	3,8

Table 21- Thermodynamic parameters for fan coil application, with a condenser temperature of 45 ºC and an evaporator temperature of 0ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	8,01	8,13	2,17	3,16	7,20	7,03
Temperature inlet compressor [ºC]	5,00					
Condenser output enthalpy [kJ/kg]	253,5	275,3	255,0	254,9	268,3	268,6
Compressor inlet enthalpy [kJ/kg]	426,75	521,37	388,61	367,93	470,17	472,73
Compressor output theory enthalpy [kJ/kg]	500,30	573,34	415,47	391,62	516,78	514,13
Compressor output real enthalpy [kJ/kg]	531,83	595,61	426,98	401,78	536,76	531,87

Compressor inlet entropy [kJ/(kg·K)]	1,83	2,18	1,69	1,61	2,00	1,99
COP	2,4	3,8	4,0	3,9	3,6	4,0

Table 22- Thermodynamic parameters for fan coil application, with a condenser temperature of 45 ºC and an evaporator temperature of 7 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	9,95	10,12	2,78	3,98	8,95	8,74
Temperature inlet compressor [ºC]	12,00					
Condenser output enthalpy [kJ/kg]	253,5	275,3	255,0	254,9	268,3	268,6
Compressor inlet enthalpy [kJ/kg]	428,98	522,79	393,48	372,59	472,79	474,98
Compressor output theory enthalpy [kJ/kg]	494,84	564,66	415,60	392,08	511,13	508,47
Compressor output real enthalpy [kJ/kg]	523,07	582,61	425,07	400,44	527,56	522,82
Compressor inlet entropy [kJ/(kg·K)]	1,82	2,15	1,69	1,62	1,98	1,98
COP	2,5	4,6	4,8	4,7	4,2	4,7

Table 23- Thermodynamic parameters for fan coil application, with a condenser temperature of 45 ºC and an evaporator temperature of 12 ºC

	R410A	R32	R1234ze	R1234yf	R452b	R454b
Evaporator pressure [bar]	11,54	11,74	3,30	4,66	10,39	10,13
Temperature inlet compressor [ºC]	17,00					
Condenser output enthalpy [kJ/kg]	253,5	275,3	255,0	254,9	268,3	268,6

Compressor inlet enthalpy [kJ/kg]	430,36	523,52	396,92	375,87	474,46	476,37
Compressor output theory enthalpy [kJ/kg]	491,03	558,68	415,78	392,49	507,24	504,56
Compressor output real enthalpy [kJ/kg]	517,02	573,74	423,86	399,61	521,29	516,64
Compressor inlet entropy [kJ/(kg·K)]	1,81	2,13	1,69	1,62	1,97	1,96
COP	2,7	5,3	5,6	5,4	4,8	5,5

The following graphs show the same COP results in different representations [Figure 9 and Figure 10] obtained for the different fluids in the different conditions described.

In order to determine the best option, the graphs of the previous data have been made. Firstly, the COP vs. the evaporator temperature of the different refrigerants [Figure 9] has been represented, and secondly, the COP vs. the different applications [Figure 10]. For both graphs show that for the three applications all the alternatives proposed have a greater COP than R410A.

In addition, for the three applications the fluids R454b and R1234ze(E) have a close value and give rise to the highest values.

To determine which refrigerant is best used the REFPROP program for calculate the latent heat and vapour density. Fluids with lower values of latent heat is need more flow and fluids with lower vapour density are required a larger unit, therefore the price increases, so with the information of the Table 24 is determined that the best alternative is R454b.

Table 24-Vapour density and latent heat measured at 5 ºC

	Vapour density [kg/m^3]	**Latent heat [kJ/kg]**
R1234ze(E)	16,37	177,74
R454b	27,81	245,19

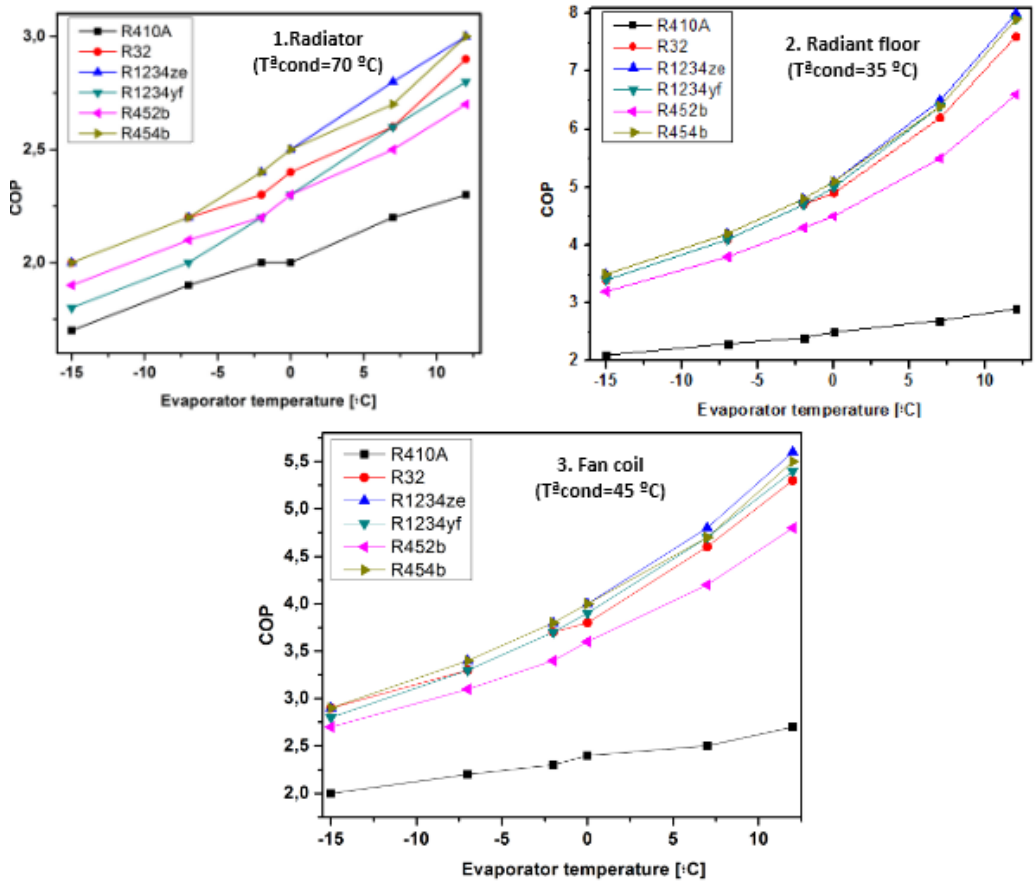
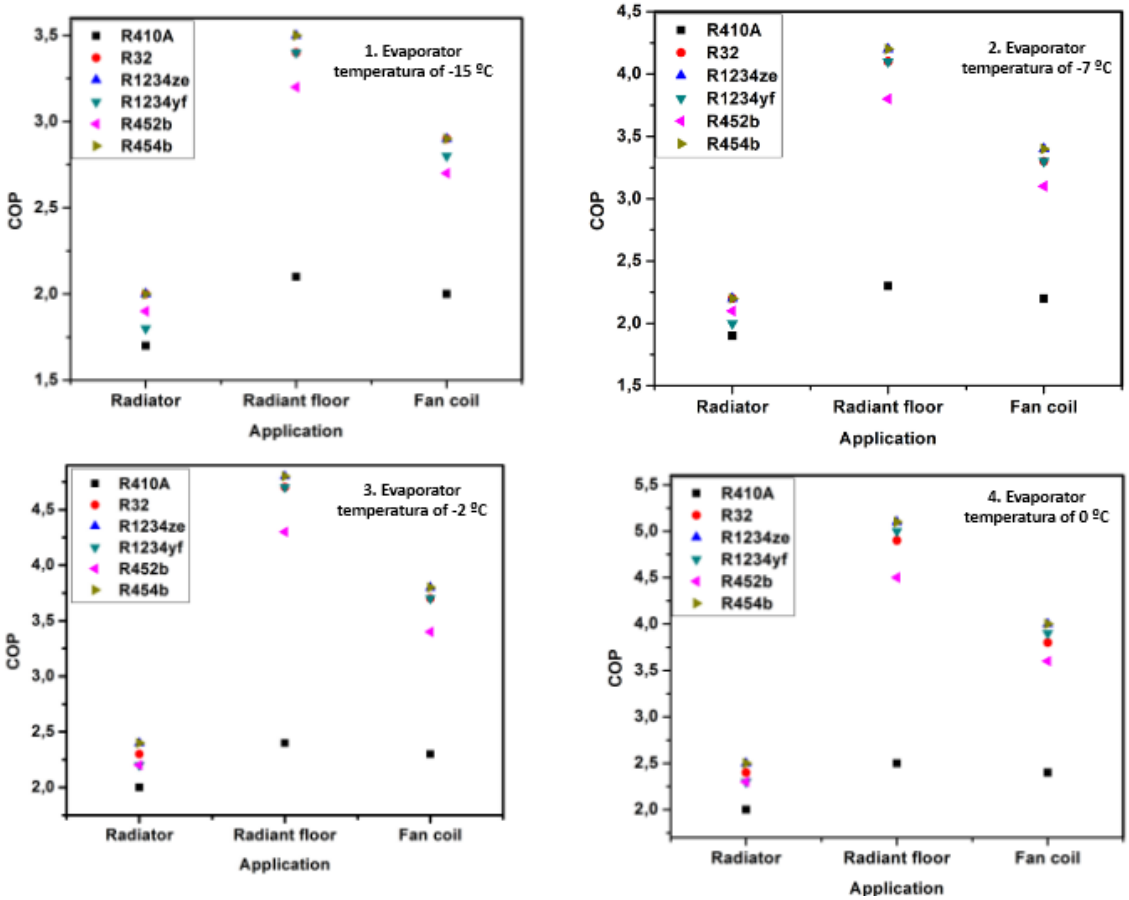


Figure 9 -COP for the different fluids and applications (1)



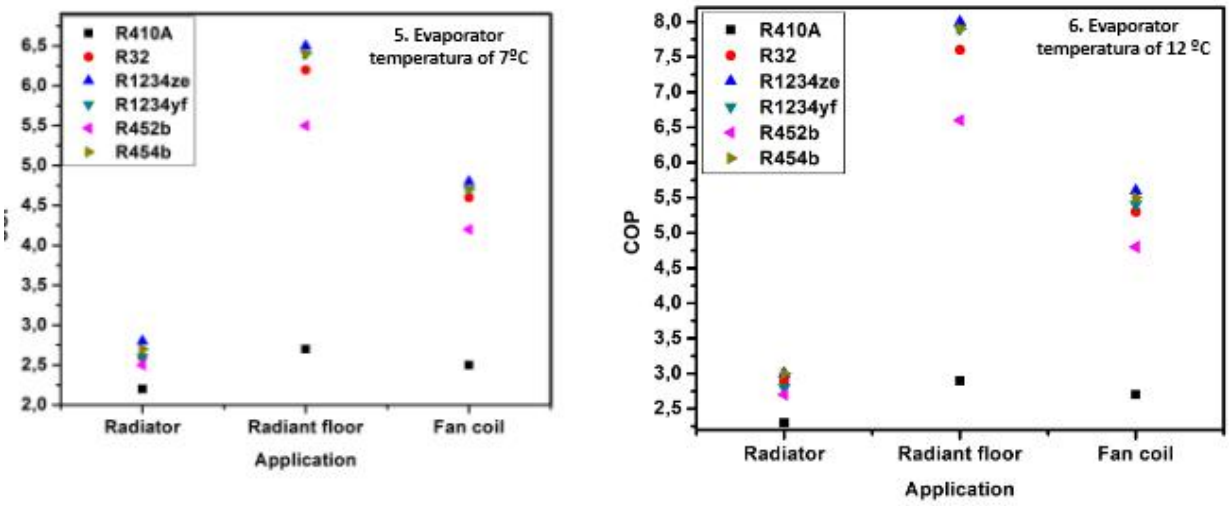


Figure 10- COP for the different fluids and applications (2)

3 Risk Assessment of R454b

In this point a chemical process quantitative risk analysis is carried out. This analysis is a probabilistic methodology designed to evaluate overall process safety in the chemical process industry. Management systems such as engineering codes, checklists and process safety management provide layers of protection against accidents.

However, the potential for serious incidents cannot be totally eliminated. It provides a quantitative method to quantify risk and analyze potential risk reduction strategies. [37]

This risk analysis has been carried out for a heat pump, this one is characterized by a power of 50 kW, the most common heat pump used today. Two hypothetical scenarios are considered:

1. The heat pump is located outdoors in an urban area
2. The heat pump is in a 20 m^2 room

The pump is used in coil fan, when the condenser temperature is 45 ºC and a evaporate temperature is 0 ºC.

3.1 Risk analysis in the first scenario: The heat pump is located outdoors

The first step is calculated the mass flow rate of gas that leaks. The mass flow has been calculated for the six different evaporator temperature studied above.

To calculate the mass flow, it is necessary to check if the flow is independent of the downstream pressure (P_2) is dependent only on the upstream pressure (P_1). This one occurs when the velocity of the discharging gas reaches the sonic velocity due to the upstream pressure decreases (or downstream pressure decreases). In order to determine if the flow regime is sonic or subsonic, the following expression is used:

$\frac{P_{chocked}}{P_1} = \left(\frac{2}{k+1}\right)^{k/(k-1)}$, If $P_{chocked}$ is less than P_2, the flow is subsonic through the hole.

For this case the downstream pressure is the atmospheric pressure (1 bar), because it is a gas that leaks to the outside. And the upstream pressure is the pressure at the condenser.

In the thesis have been calculated for the three applications described above. So, the condenser temperature is the initial upstream temperature of the gas and it is studied for the values of 70,35 y 45 ºC.

Table 25-Dates used to calculate the $P_{chocked}$ T_{evap} = 0 ºC and P_2= 1 bar

Condenser temperature [ºC]	Condenser temperature [K]	Condenser pressure, P_1 f($T_{condenser}$) [MPa]*	k=C_p/C_v f(P_c, Tc)*	$\left(\frac{2}{k+1}\right)^{k/(k-1)}$	Chocked pressure [bar]
75	348,15	0,5	1,200	0,564	13,49
35	308,15	0,19	1,202	0,564	13,48
45	318,15	0,24	1,200	0,564	13,49

*These dates are obtained using the REFPROP program

As P_2 is less than $P_{chocked}$ in all cases, the flow is sonic through the hole. For sonic gas flow discharges used the following expression. This one assumes an ideal gas and no heat transfer.

$$\dot{m} = C_D \cdot A \cdot P_1 \cdot \sqrt{\frac{k \cdot g \cdot M}{Rg \cdot T_1}\left(\frac{2}{k+1}\right)^{(k+1)/(k-1)}}$$

where

- $\dot{m}$ is mass flow rate of gas through the hole (mass/time)
- C_D is the discharge coefficient (dimensionless). It supposed a standard value of 0,62
- A is the area of the hole (m^2).

It supposed a 10 mm hole diameter, $A = \frac{\pi \cdot D^2}{4}$=7,85·10-5 m^2

- P_1 is the pressure upstream of the hole (Pa)
- g is the gravitational constant (force/mass-acceleration)
- M is the molecular weight of the gas (mass/mole)
- k is the heat capacity ratio, C_p/C_v (unitless)
- R_g is the ideal gas constant (pressure-volume/mole-deg)
- T_1 is the upstream temperature of the gas (deg). This one is the condenser temperature.
- P_2 is the downstream pressure (Pa)

The mass flow for the different conditions explained above are in the next table [Table 26]

Table 26- Mass flow of R454b fluid for different ambient temperature [ºC]

Condenser temperature [ºC]	Mass flow [kg/s]
75	**4,22**
35	**4,47**
45	**4,42**

Once the flow rate is known, the model for continuous discharges is applied: **Plume Model**. This model depends on the rate of release, the atmospheric conditions, the height of the release. It supposes that the wind is moving at a constant speed, in the x

direction: This model is accurate from 100 m to 1 km from the leak exit. So, the concentration has been measuring for that range. Its idea is reflected in Figure 11. [37]

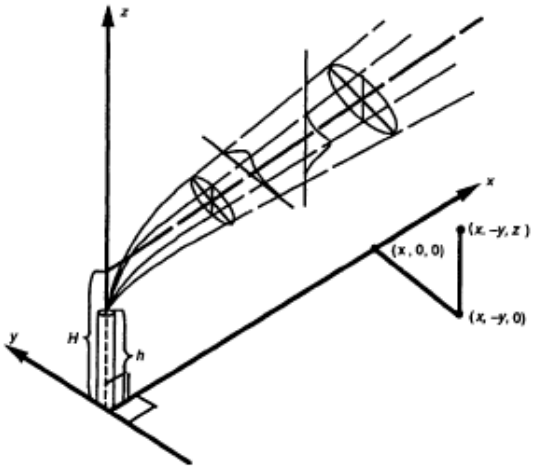


Figure 11- Plume Model idea [37]

The equation that this model rife is based on:

$$C(x,y,z) = \frac{G}{2 \cdot \pi \cdot u \cdot \sigma_y \cdot \sigma_z} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \left\{\exp\left(\frac{-(z-H)^2}{2\sigma_z^2}\right) + \exp\left(\frac{-(z+H)^2}{2\sigma_z^2}\right)\right\}$$

where

- C(x,y,z) is the average concentration (mass/volume),
- G is the continuous release rate (mass/time). As for the three applications a similar flow has been obtained, the average value of these will be used: 4,3 kg/s
- σ_x, σ_y and σ_z are the dispersion coefficients in the x, y, and z directions (length). They depend of the stability class.

In this case it assumed neutral stability class: type D that is governed by the following parameters.

Table 27- Pasquill parameters for neutral stability

Stability neutral class. Type D	
A	0,128
B	0,905

C	0,2
D	0,76

$\sigma_y=a\cdot x^b$ y $\sigma_z=c\cdot x^d$

- u is the wind speed (length/time). It has been assumed a value of 5 m/s
- y is the cross-wind direction (length)
- z is the distance above the ground (length). The z-coordinate has been assumed that is equal to the average human height (1,7 m).
- H is the height of the source above ground level plus plume rise (length)

Moreover, for this thesis it assumed that the fluid releases at ground level, z=0, the maximum concentration occurs at the release point.

With the previous simplifications the expression to use has the form of:

$$C(x,0{,}1'7)=\frac{G}{\pi\cdot 5\cdot\sigma_y\cdot\sigma_z}\left[\exp\left(\frac{-(1{,}7)^2}{2\sigma_z^2}\right)+\exp\left(\frac{-(1{,}7)^2}{2\sigma_z^2}\right)\right]$$

The following figures [Figure 12] show how the concentration change according to the distance the person is at.

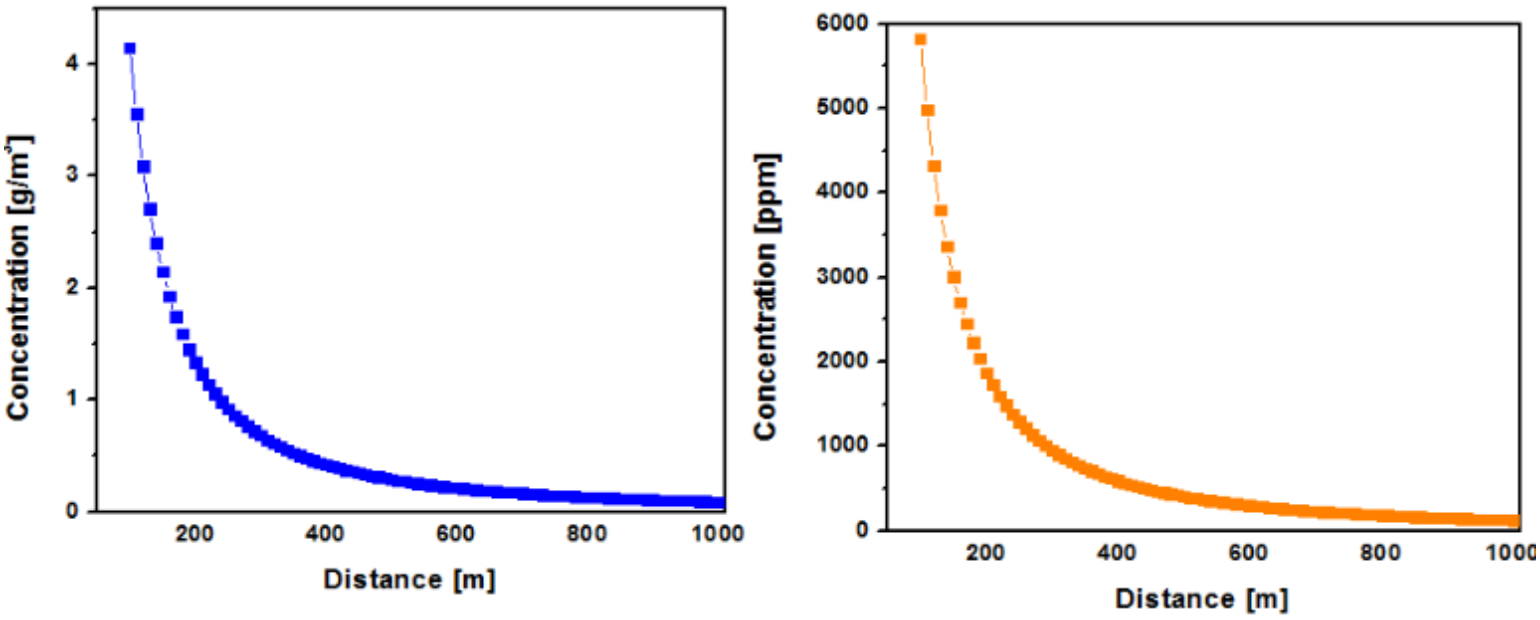


Figure 12- R454b concentration vs distance [g/m³] and [ppm]

A fluid has a risk of ignition if it must be between two limits as explained in the introduction. Searching in bibliography [38] it is known that for the fluid R4545b the minimum concentration is 300 g/m^3. In this case, the concentration is below this lower value, so under these conditions there would be no ignition.

3.1.1 Jet fire

As indicated in the introduction, this fluid is characterized by a mildly flammable. Its upper flammability limit is 22% (vol) and its lower limit is 11,25 % (vol). So, due to this characteristic, the fluid can ignite. It is interesting to study how its jet fire. [39] The jet fire is common result from the combustion of a material as it is being released from a pressurized process unit. The main concern is in local radiation effects.

The first step is calculated the fire height, it assumed that it is a vertical flame. It used the next expression:

$$\frac{L}{d_j} = \frac{5{,}3}{C_T}\sqrt{\frac{T_f/T_j}{\alpha_T}\left[C_T + (1 - C_T)\frac{M_a}{M_f}\right]}$$

where

- L is the length of the visible turbulent flame measured from the break point (m)
- d_j is the diameter of the jet, that is the physical diameter of the nozzle (m)
- C_T is the fuel mole fraction concentration in a stoichiometric fuel-air mixture

(unitless)

In this case assumed that the reaction is complete

$$0{,}83CH_2F_2 + 0{,}17C_3H_2F_4 + 2{,}42\ O_2 + 9{,}1N_2 \rightarrow 1{,}34CO_2 + H_2O + 1{,}17F_2O + 9{,}1N_2$$

- T_f and T_j are the adiabatic flame temperature and jet fluid temperature, respectively (K)
- α_T is the moles of reactant per mole of product for a stoichiometric fuel-air

mixture (unitless)

- M_A is the molecular weight of the air (mass/mole). 29 kg/kmol
- M_f is the molecular weight of the fuel (mass/mole). 62,614 kg/kmol

For most fuels, C_T is typically much less than 1, α_T is approximately 1, and the ratio T_f/T_j varies between *7* and 9. In this thesis these assumptions are applied and resulting in the following simplified equation:

$$\frac{L}{d_j} = \frac{15}{C_T}\sqrt{\frac{M_a}{M_f}} \rightarrow \mathbf{L} = 0{,}01 \cdot \frac{15}{0{,}079}\sqrt{\frac{29}{62{,}61}} = \mathbf{1{,}28\ m}$$

To calculate this radiation depending on the distance from the receiver [Figure 13] is used the following equation: [37]

$$E_r = \tau_a \cdot Q_T \cdot F_P = \tau_a \cdot \eta \cdot \dot{m} \cdot \Delta H_C \cdot F_P$$

where

- E_T is the radiant flux at the receiver (energy/area-time)
- τ_a is the atmospheric transmissivity (unitless) is calculated used the following expression:

$$\tau_a = 2{,}02[P_w \cdot x]^{-0.09};\ P_w = RH \cdot P_{vap.water}.\ \text{It tought ar elative humidity}(HR) = 50\%$$

- Q_T is the total energy radiated by the source (energy/time)
- F_P is the point source view factor (m^2). It provided by the next equation:

$$F_P = \frac{1}{4\pi x^2},\ \text{the radiation path length } (x) \text{is the length of the hypotenuse [Figure 13]}$$

- η is the fraction of total energy converted to radiation (unitless). It has not found. So, it takes an arbitrary value of 0,25. Due to according to literature the normal range of this value is between 0,15-0,4.
- m is the mass flow rate of the fuel (mass/time). It calculated above.
- ΔH_C is the energy of combustion of the fuel (energy/mass).

As the R4545b is relatively a new fluid, it has not been possible to find its combustion enthalpy in the literature. So, it has been calculated using the reaction of that takes. The reactants of combustion are the two components of this refrigerant: R-32 (CH_2F_2) and R-1234yf ($C_3H_2F_4$). And it has been assumed that a complete reaction takes place:

$$0{,}83CH_2F_2 + 0{,}17C_3H_2F_4 + 2{,}42\ O_2 + 9{,}1N_2 \rightarrow 1{,}34CO_2 + H_2O + 1{,}17F_2O + 9{,}1N_2$$

The combustion enthalpy is calculated as the energy difference between products and reactants obtained by the EES program.

$$h_{combustion} = n\sum h^{o}_{product} - m\sum h^{o}_{react} =$$

$$= (1{,}17 \cdot 24{,}5 + 242 + 393{,}77 \cdot 1{,}34) - (0.83 \cdot 234.04\ + 0{,}17 \cdot 165{,}8) = \mathbf{523{,}88\ kJ/mol}$$

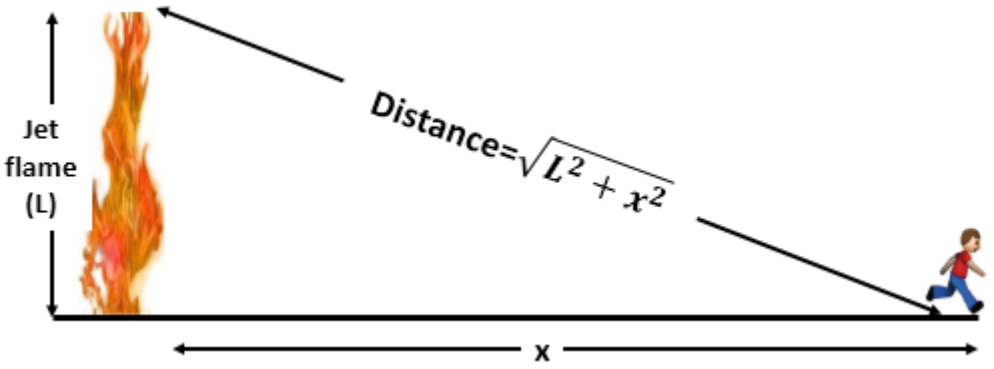


Figure 13- Jet set sketch

The following graph [Figure 14] shows how the radiant flux is in function of the distance. It is observed that at 10 meters from the leak there is no radiation. Therefore, under the described conditions, a leakage of the fluid would not have serious consequences unless an operator is in these moment next to the pump.

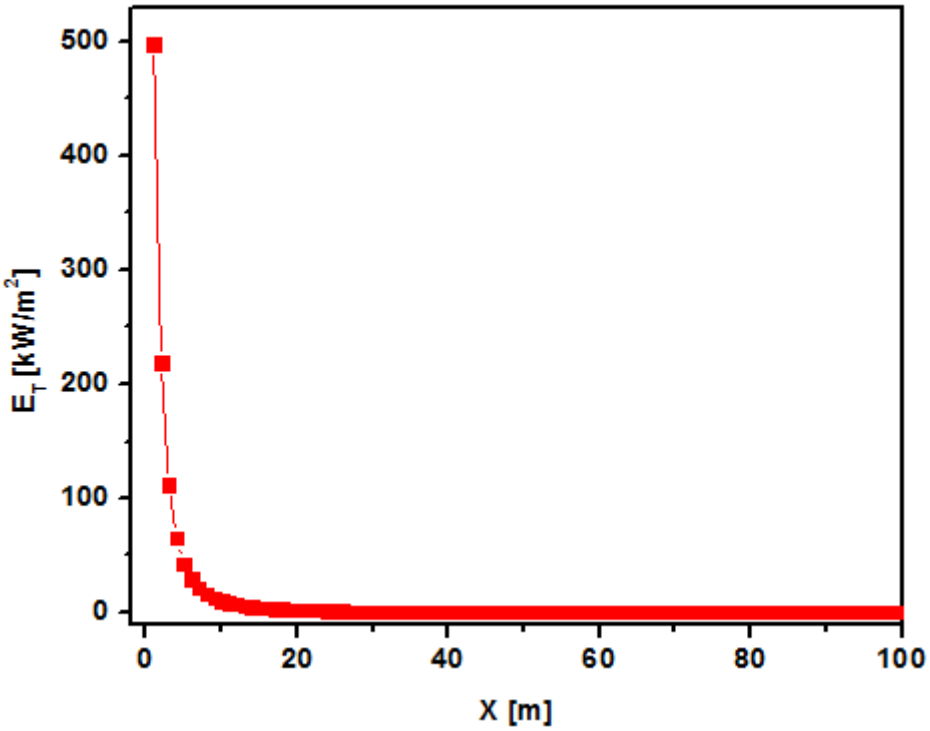


Figure 14 - Radiant flux vs distance

3.2 Risk analysis in the second scenario: The heat pump is in a room of 20 m^2

This scenario has been studied in the worst-case, all the fluid leaks. For this purpose, a heat pump catalogue was used to know how much refrigerant mass is used for a 50 kW heat pump:11 kg. [40]

It has been assumed that the heat pump is situated in a room of 20 m^2 as the Figure 15. The concentration in that room once the gas has leaked is:

$$\text{Concentration} = {}^{\text{mass}}/_{\text{Vol}_{\text{room}}} = {}^{11000}/_{20} = 550\,\frac{\text{g}}{\text{m}^3}$$

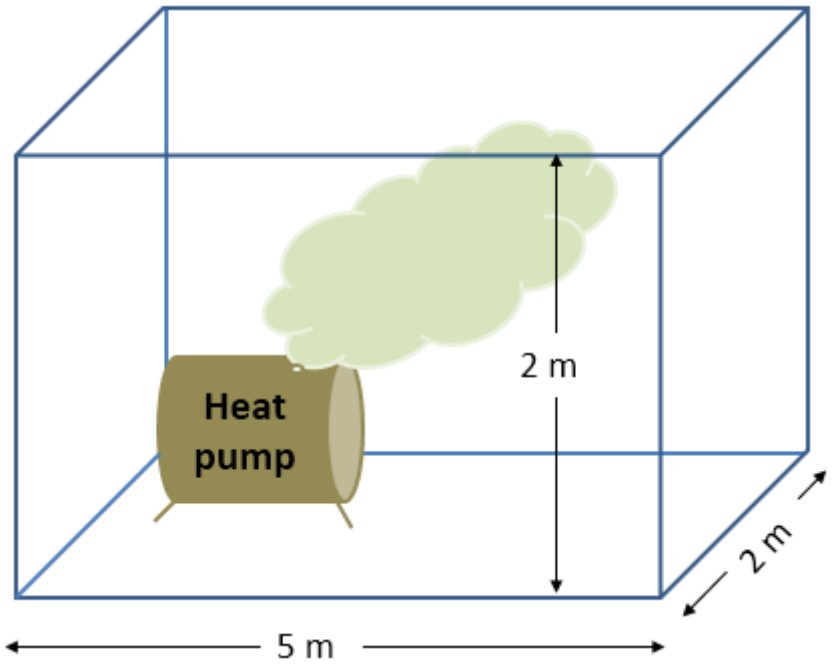


Figure 15- Risk assessment of the second scenario

The acute toxicity exposure limit (ATEL) of any refrigerant may also applied as a constraint to the amount of refrigerant that can be released into a room or enclosure, as it represents the smallest quantity that could impose adverse toxicological effects onto occupants. For this fluid the **ATEL equal to 435 g/m^3**. [38]
In order to avoid poisoning in the unwanted event of a leak in the installation, if the amount of refrigerant used is optimal, the size of the room where the heat pump is located should be considered. Minimum amplify this size to a volume of 26 m^3, to be below this ATEL value.

Another value to keep in mind is the practical limit (PL) in a room. This is a further safety measure for the application of refrigerants and represents the highest concentrations level in an occupied space which will not result in any escape impairing effects that, it is mean that the lowest dangerous concentration of the fluid. For this fluid its value is **60 g/m^3** [38]
The value obtained for this total fluid leakage is above this value. So, a leak in these conditions would be dangerous for the workers present.

4 Conclusions

This paper has investigated an alternative to refrigerant R410A for its use in heat pumps. For this purpose, five refrigerants have been studied and compared according to their performance: COP, for a heat pump. For the different alternatives, R454b fluid has been chosen as the best option because the COP obtained is the one with the highest value for all the situations presented: different applications of the heat pump and different temperatures of the evaporator.

In addition, the risk analysis carried out with the R454b fluid in an outdoor scenario with a 50 kW heat pump in the event of a leak. There is no danger of ignition and that under these conditions 200 meters from the leak the concentration of this refrigerant is close to zero. It is concluded therefore that they are safe conditions for a human. However, for the second proposed scenario: a 20 m^2 room where in the heat pump there is a total leakage of the fluid. If an employer, who would be in the room at the time of the leak, could suffer from intoxication. Due to the acute toxicity exposure limit for these refrigerants is 435 g/m^3 and for the conditions described the concentration obtained is 550 g/m^3.

Due to this conclusion, future work should determine what conditions the room where the pump is located should have so that the unfortunate case of leakage does not involve human intoxication. Moreover, the different alternatives should be compared using as a comparative method more than just their COP.

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